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The specific heats of crystals and the fallacy of the theories of Debye and Born

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1. Introduction

The first step in any attempt at a theoretical evaluation of the specific heats of crystals is to determine the nature of the disturbance in their structure produced by the thermal agitation. In an earlier publication[1] and more fully again in the address to the Conference of Nobel Laureates held at Lindau in June 1956 which was printed in these *Proceedings*,[2] this problem was discussed. A general theory of the specific heats of crystals embodying the ideas expressed in those memoirs has since been formulated and published.[3] The theory leads to a determination of the spectroscopic behaviour of crystals and simultaneously with it to an expression for their specific heats as a function of the temperature. The success of the theory in achieving these aims has been demonstrated by a series of fully worked-out examples and a comparison with the facts of experiment.[4]

The principles on which the present approach to specific heat theory is based may be briefly sketched here. While the classical mechanics is made use of in the theory, stress is laid on the necessity of paying due regard at the same time to the basic principles of thermodynamics and to the fundamental notions of the quantum theory. With these requirements in view, the crystal is regarded as an assembly in thermodynamic equilibrium of sets of *similar* oscillators in great number, the energies of vibration of which are *individually* quantised. The identification and enumeration of these oscillators and the determination of their modes and frequencies of vibration is accomplished by taking note of the three-dimensional periodicity of structure characteristic of crystals and applying to the elements of that structure essentially the same methods as those which are so successful in the field of molecular spectroscopy. The determination of the thermal energy of the crystal as a function of the temperature is then effected by the same procedure as that indicated by Einstein in his fundamental paper[5] of 1907 introducing the quantum theory of specific heats.

The present approach to specific heat theory rejects completely the ideas regarding the subject embodied in Debye's well known paper[6] and also those set out by Born and his school in numerous publications.[7] As the present generation of physicists and chemists has been brought up to believe in these latter theories, it would not be superfluous to explain in some detail why their rejection is necessary. That indeed is the purpose of the present memoir, which is sought to be achieved by a searching examination of the premises underlying the theories of Debye and Born and of the consequences to which those theories lead. It emerges from the examination that those premises are untenable and that the conclusions derived from them are false.

2. The hypothesis of Jeans

The parent of the specific heat theories of Debye and Born and also of other similar theories was a publication[8] by J H Jeans which appeared in the *Philosophical Magazine* in the year 1909. Though the title of that paper indicated temperature radiation as its subject, actually it was devoted for the most part to a discussion of the thermal behaviour of material bodies on the basis of classical mechanics. It put forward and sought to establish a proposition which may be stated as follows: *the thermal energy of material bodies is identifiable with the sum of the potential and kinetic energies of regular trains of waves traversing them and forming stationary wave-patterns filling their volume.* The reader familiar with Debye's specific heat theory will immediately recognise this as the thesis which Debye accepted and elaborated in his attempt to explain the experimental results for the specific heats of elementary solids at low temperatures. It is not surprising in these circumstances that Jeans became an enthusiastic supporter of Debye's theory and by his advocacy helped to promote a general belief in the validity of the thesis on which that theory was based.

The waves considered by Debye in his paper were the longitudinal and transversal waves in an isotropic solid contemplated by the classical theory of elasticity. The formulae set out in the paper were based on an analysis of the modes of vibration of an elastic solid sphere whose external surface was assumed to be rigidly fixed, followed by their enumeration in terms of their frequencies of vibration. Debye restricted himself for the most part to a consideration of the cases of monatomic solids exhibiting cubic symmetry. No such restriction is contemplated in the theory put forward and developed by Born and his school, which claims to be valid for all crystals. While Debye considered it to be adequate for his purpose to regard the vibrating solid as a continuum, the Born theory claims to take account of the discrete lattice structure of the crystal. The waves considered in it are also of more general kind than those recognised by Debye. Nevertheless, the theory of Born, like that of Debye, is based on an acceptance of the same thesis, viz., the hypothesis of Jeans.

3. The fallacy of the hypothesis

Simple considerations of a general character suffice to show that the hypothesis of Jeans is a wholly misconceived idea. We have only to remark that the specific heat of a solid is an atomistic property, since its value at any given temperature is completely determined by two quantities, one of which is the number of atoms comprised in unit mass of the substance, and the other is the effective average frequency of vibration of the atoms at that temperature. Any attempt to explain this situation theoretically has, of necessity, to base itself on an atomistic approach to the problem. In other words, we have to consider the individual atoms in the crystal and investigate their dynamic behaviour. *Per contra*, wave-motions and the stationary wave-patterns resulting from the presence of an external boundary limiting their travel are macroscopic concepts, which, it should be emphasised, do not require us to take any notice of the atomicity of structure of the material traversed by the waves. In these circumstances, it is obvious that the attempt to build a theory of specific heats on the assumption that the thermal agitation is identifiable with wave-motions is an illogical and illusory proceeding.

We may usefully enlarge upon the foregoing remarks. The specific heat theories based on the hypothesis of Jeans concern themselves with the enumeration of the stationary wave-patterns assumed to exist within the volume of the solid. But, since the atomicity of structure of the material need not at all be considered in the description and enumeration of the wave-patterns, it remains completely outside the problem. The identification of the thermal energy of the solids with the sum of the kinetic and potential energies of the wave-patterns is therefore incapable of leading us to any determination of their specific heats. The difficulty which arises here is one of pure logic and is fundamental. In the theories now under discussion, the difficulty is sought to be circumvented by introducing an additional assumption, viz., that the total number of wave-patterns is equal to thrice the number of atoms comprised in the crystal. While this assumption may appear plausible, it cannot be pretended that such a fixation of the number of wave-patterns is a necessary consequence or concomitant of the wave hypothesis. Actually, of course, it is introduced in order "to make the theory work", in other words, in order that the results of the theory might bear some resemblance to the experimental facts. In logic, such a proceeding would be described as *petitio principii*, or begging the question.

4. Thermodynamics and the theory of specific heats

It can be readily shown that the notions underlying the theories of Debye and Born are irreconcilable with the statistical concept of the nature of thermal energy which lies at the very base of the science of thermodynamics. A crystal is an assembly of an immense number of individual atoms which are capable of moving from their positions of equilibrium. Hence, the state of the system can only be described in terms of the values of a very large number of independent variables. No doubt, the atoms are held together by their mutual interactions to form the ordered assemblage which we call a crystal and which can be regarded as a unit in the macroscopic sense. But the statistical concept of thermal energy forbids us from regarding the entire assembly as a single unit in the thermodynamic sense. We cannot, for example, identify the thermal energy of the crystal with the energy of stationary wave-patterns of any sort. Indeed, the constancy of amplitude and coherence of phase relationship over extended regions of space and large periods of time which the formation of such wave-patterns presupposes are excluded by reason of the very nature of thermal energy. *Per contra*, it is to be expected that the thermal energy of a solid exhibits fluctuations in space and in time which preclude any definitive description of it except for domains of space and periods of time which are very small in comparison with macroscopic standards.

5. Classical mechanics and the theory of specific heats

That the theories of Debye and Born are untenable become evident also when we examine them from the standpoint of classical mechanics. For, specific heat theory starts from the well known theorem that all the possible vibrations of a system of connected particles are superpositions of a set of normal modes in each of which the particles oscillate with the same frequency and in the same or opposite phases. The particles in the present problem are the individual atoms in the crystal and hence we are here concerned with the determination of the normal modes of vibration of *the atoms* in the sense of the theorem just stated. Instead of considering this question, the theories of Debye and Born concern themselves with an entirely different and indeed irrelevant subject, viz., the normal modes of vibration of a macroscopic solid as determined by the form of its external boundary. Their treatment of specific heat theory thus stands revealed as a purely fanciful approach devoid of any validity or significance.

A straightforward application of the standard methods of classical dynamics enables us to determine the characteristic modes and frequencies with which the atoms in a three-dimensionally periodic array can oscillate about their positions of equilibrium. It emerges from the investigation that these characteristic modes can be enumerated and that they are related in a precisely definable manner to the structure and symmetry properties of the atomic groupings in the crystal. In the theories of Debye and Born, on the other hand, which assume that the modes of vibration are determined by the external boundary conditions and further, that the total number of wave-patterns is equal to thrice the number of atoms included in the crystal, we encounter results of an altogether different character. According to these theories, the great majority of the stationary wave-patterns which they contemplate have "wavelengths" of the same order of magnitude as the lattice-spacings of the crystal. But these wavelengths are all different and represent different frequencies of vibration. As a consequence, the "cells" of the wave-pattern in which the phase of vibration alternates bear no relation whatever to the structure of the crystal, while the wave-patterns themselves appear in immense numbers and are all different from each other. Such a description of the dynamical behaviour of the atoms linked with one another in the geometrically ordered structure of a crystal is, on the face of it, a fantastic misrepresentation. It is, in effect, a *reductio ad absurdum* of the theories which lead up to it.

6. The quantum theory of specific heats

The ideas which connect the hypothesis of energy quanta with the theory of specific heats were very clearly expounded in Einstein's classic paper[5] of 1907. If it be assumed that radiation is emitted or absorbed in energy-quanta proportional to the frequency, it follows as a necessary consequence that the mechanical energy of the oscillator which thus emits or absorbs would itself diminish or increase respectively by finite steps of the same amount. Generalising this result, Einstein postulated that the energy of any elementary structure capable of mechanical vibration would likewise obey the quantum rule. He then coupled this with the concept of thermodynamic probability embodied in Boltzmann's principle and showed that the relative probabilities of the oscillator being in different energy states could be determined with the aid of the principle. The next step is the evaluation of the average energy of an oscillator in an assembly consisting of a great number of such oscillators having a common frequency of vibration. This leads at once to the evaluation of the thermal energy of the whole assembly. The basic ideas of the quantum theory were further clarified and illumined by Einstein in the famous paper[9] of 1917 in which he showed that the exchange of energy between a radiation field and the oscillators located in it can properly be described only in terms of statistical concepts. The probability of the oscillator being in any given state appears in the paper as the product of two factors, one of which is the thermodynamic probability factor given by the Boltzmann formula and the other is the intrinsic statistical weight of that state.

The foregoing remarks are made to emphasise that the quantum theory of specific heats rests on thermodynamic-statistical concepts which are wholly alien to the determinism of macroscopic physics. In other words, the theory of energy-quanta possesses a meaning and significance only in relation to the behaviour of the ultimate units of which matter is composed; *per contra* it is wholly out of place in any considerations regarding the behaviour of matter in bulk. For example, we can speak of the energy states of rotation or vibration of a molecule of benzene, but it would be nonsensical to discuss the problem of quantising the vibration of a tuning fork or the rotations of a fly-wheel.

It will be clear from the foregoing remarks that Debye and Born fell grievously into error when they rejected the basic ideas of Einstein's theory and sought to build a theory of the specific heats of crystals on the behaviour of macroscopic solids. In doing this, not only did they ignore all considerations of logic as well as the physical principles bearing on the subject, but they also sought to impose on the quantum theory a fantastic and altogether meaningless interpretation.

7. The spectroscopic behaviour of crystals

The specific heats of crystals and their spectroscopic behaviour are intimately related properties since they are both determined by the frequencies of vibration of the atoms about their positions of equilibrium. This relationship is conveyed more precisely by the statement that the elementary oscillators in the crystal which are the carriers of its heat energy are also the oscillators capable of absorbing, emitting or scattering the radiations incident on it. It follows that any valid specific heat theory contains within itself a complete description of the vibration spectrum of a crystal: vice versa, a theory of the spectroscopic behaviour of crystals which correctly describes the facts of observation in that field necessarily contains within itself all the data needed for the evaluation of the specific heat as a function of the temperature.

From the foregoing remarks, it follows that the theories of Debye and Born which are based on erroneous assumptions regarding the carriers of the thermal energy in crystals also lead to a false picture of their vibration spectra. That is actually the case, for the assumptions made in these theories lead to the conclusion that the vibration frequencies of a crystal are immensely numerous and are all different from each other and hence that the vibration spectrum exhibits a continuous band of frequencies stretching over the entire range. *Per contra*, the atomistic theory of specific heats shows that the vibration spectrum of a crystal consists of a finite number of discrete monochromatic frequencies accompanied by a residual spectrum with a relatively small statistical weight which may be considered as continuous and which goes down to very low frequencies.

Spectroscopy is an exact science, and the vibration spectra of crystals are accessible to precise study and investigation by several different techniques and with a great variety of materials. In every case, the experimental results support and confirm the results of the atomistic theory in an unequivocal fashion. They are therefore also an objective demonstration of the falsity of the Debye and Born theories.

8. Summary

It is shown that the hypothesis, originally proposed by Jeans and adopted in the theories of Debye and Born, that the thermal energy of a solid is identifiable with the energy of wave-motions in its interior is not logically sustainable as a basis for a theory of their specific heats. The constancy of amplitude and of phase-relationships in extended volumes and periods of time demanded by the hypothesis is irreconcilable with the statistical-thermodynamical concept of the nature of thermal energy, and the idea that the theory of specific heats can be treated as a boundary-value problem in the physics of macroscopic solids is therefore misconceived. It is shown that such an approach is repugnant both to classical mechanics and to the principles of the quantum theory. It must therefore give place to a purely atomistic approach which gives us a wholly different picture of the nature of the thermal agitation in the solid and of its vibration spectrum.

References

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